

thought to arise from the cyclized carbon attached to the exocyclic methylene (carbon 8). The peaks resonating at 127ppm and 138ppm in the spectrum of the Yallourn resinite have been assigned to the protonated (carbon 12) and quaternary (carbon 13) carbons of the side chain double bond by chemical shift comparisons with model compounds (27-28) and by previously reported dipolar dephasing experiments (12). Relative peak areas for each resonance in the olefinic region as well as the total olefinic carbon content of the spectra indicate that the total olefinic content, in a 20 carbon structural unit, progressively decreases from approximately 4 carbons per monomer in the spectrum of the Yallourn resinite to approximately 2 carbons per monomer in the spectrum of the Brunner resinite. As the thermal maturation of the resinite increases, there is a decrease of nearly 50% for the olefinic carbons in the samples being studied. This loss corresponds to the transformation of diterpenoids containing two double bonds (polycommunic acid units) to diterpenoids having only one double bond.

Integration of the carboxylic acid resonances, peaks at 186ppm and 181ppm, of the spectra of the Yallourn and Morwell resinites and 186ppm, 181ppm and 177ppm for the spectrum of the Brunner resinite, yielded values of 0.8, 0.7, and 0.5 carbons per monomer, respectively. As the degree of maturation increases, there appears to be a decrease in intensity of the peaks resonating at 186ppm and 181ppm with an additional resonance in the carboxyl region centered around 177ppm visible in the spectrum of the Brunner resinite. The broad peak resonating between 201ppm and 210ppm in the spectra of the Morwell and Brunner resinites has been assigned to ketones resulting from oxidation (18).

The intramolecular cyclization of the exocyclic methylene to form a mono-unsaturated C ring (Figure 2), is entirely consistent with pyrolysis and NMR data. The positioning of the double bond between carbons 8 and 17 (of the communic acid monomer) will stabilize the B and C rings thus making cleavage of the A ring rather than the B or C rings the more likely site of pyrolysis. The compound(s) expected to dominate the pyrolysis of a polymeric tricyclic acid (as described above) are alkyl naphthalenes and alkyl hydronaphthalenes. With this information, the combined results of the quantitative NMR data and py/gc/ms data, it is possible to rule out proposed mechanisms of maturation other than that of intramolecular cyclization which appears to correlate with all the chemical data.

SESQUITERPENOID-TYPE RESINITES

The general consensus regarding the structure of sesquiterpenoid resinites is that the maceral exists as two fractions. One fraction consists of a high molecular weight (HMW) polymer proposed to be that of polycadinene (PC)(30) and the second fraction is composed of low molecular weight compounds shown by gas chromatography/ mass spectrometry (GC/MS) to be dimers and trimers of cadinene and functionalized triterpenoids (30-32).

In this report, we will discuss the results of a series of experiments which were carried out in an effort to characterize the polymeric fraction of an immature resin, a precursor to sesquiterpenoid-based resinites. By examining the structure of polycadinene from a young resin such as a Dammar resin, we would be able to compare these structural characteristics with those of more mature resinites such as that described from the Blind Canyon coal (33-34). From this comparison the chemical changes that accompany the maturation process can be identified thus further aiding in the structural identification of the Blind Canyon coal's resinite maceral.

The Dammar resin was chosen due to its availability in a relatively pure form. In addition, this particular resin is extremely soluble in CDCl₃. Solubility in CDCl₃ was an important consideration, since NMR was chosen as the primary structural tool for this study. NMR techniques, which include one- and two-dimensional NMR spectra, were used in this study to determine the consistency of the structure of a high molecular weight methanol insoluble fraction of the Dammar resin (the polycadinene biopolymer as suggested by van Aarssen et al.(30)) with that of a theoretical polycadinene polymer and to propose possible chemical alterations induced during catagenesis.

The resin selected for this study is a commercially available Dammar resin purchased from Aldrich Chemical Co. The Dammar resin was first dissolved in 50 mL of hexane then approximately 5 mL of methanol was added to precipitate the polymer as a white powder following the procedure described by van Aarssen et. al. (30). The powder was then separated by centrifugation and washed with methanol. The methanol was evaporated and replaced with approximately 0.6 mL of CDCl₃, a solvent suitable for NMR spectroscopy.

The high resolution liquid ¹H and ¹³C NMR experiments were performed on a Bruker AMX-360 spectrometer equipped with a 5mm inverse-detected probe. The one-dimensional single pulse ¹H and ¹³C experiments were carried out using a 30° flip angle. The ¹³C distortionless polarization transfer (DEPT) experiments were carried out using 45° (3.3 μs), 90° (6.6 μs), and 135° (16.5 μs) ¹³C read pulses, respectively. A solid state ¹³C CPMAS spectrum was obtained on a Chemagnetics M-100 NMR spectrometer. The pertinent parameters are found elsewhere (33). A two-dimensional high resolution liquid experiment COSY (homonuclear correlation) with a 45°

read pulse was performed on the HMW fraction isolated from the Dammar resin using a standard Bruker experiment.

Elemental analyses of the methanol insoluble fraction of the extant Dammar resin as well as previously reported data for resinite from the Blind Canyon coal can be seen in Table 1. Included in Table 1 are the calculated oxygen and hydrogen weight percentages of a pure polycadinene polymer (structure shown in Figure 4), which has the monomeric formula $C_{15}H_{26}$, and the monomeric formula of the HMW Dammar polymer. It can be inferred from this table that the polymeric constituent of the Dammar resin does not differ significantly from that of the Blind Canyon resinite. Also evident in this table are the considerable differences between the polymer isolated from the extant Dammar resin and that of a pure polymer composed solely of cadinene monomers. The Dammar PC elemental data suggests the presence of approximately one oxygen atom for every two cadinene monomers (assuming 15 carbons per monomer) and two less hydrogen atoms than the cadinene's 26.

^{13}C NMR was used to identify the functional groups and substitution patterns of the carbons present in the polycadinene fraction of the Dammar resin. Figure 5a-d shows high resolution ^{13}C NMR spectra of the polycadinene from Dammar resin in $CDCl_3$. Figure 5a is a quantitative decoupled ^{13}C NMR spectrum, while Figures 5b-d are the ^{13}C distortionless polarization transfer (DEPT) used to aid in assigning carbon substitution. The aliphatic region of the spectrum (0 ppm to 60 ppm) is extremely complex and contains a number of sharp signals far greater than what can be anticipated for pure polycadinene. The olefinic region of the spectrum (120 ppm to 140 ppm) is not as complex, however, but it is still not consistent with the structure of a pure cadinene monomer. In cadinene, there are two olefinic carbons with one being a tertiary carbon and the other a quaternary carbon. The spectrum shows at least four peaks.

The spectra shown in Figures 5b-d are the three ^{13}C DEPT experiments (45° , 90° , and 135°). From these spectra and the spectrum in Figure 5a, the functional group assignments can be made. Chemical shift analysis of the spectrum in Figure 5a is used as a preliminary means of assigning carbon substitution, while the DEPT spectra provide a means of sorting or spectrally editing the signals. For example, the DEPT 45° spectrum contains CH_3 , CH_2 , and CH carbons with the most intense signals emanating from the CH_2 carbons. The DEPT 90° spectrum contains only CH carbons, and the DEPT 135° spectrum contains positive signals from the CH and CH_3 carbons, but negative signals from the CH_2 carbons. Thus when the results from the three DEPT spectra are combined all the protonated carbons can be assigned. The non protonated carbons are assigned by difference from the ^{13}C broadband decoupled spectrum.

To further aid in the structural elucidation of the Dammar HMW resin polymer, two dimensional (2D) NMR data was obtained. 2D-NMR is capable of correlating and spreading out NMR spectral data thus providing a means of confirming one dimensional spectral assignments while at the same time providing structural information concerning molecular connectivity. The 1H-1H correlation spectrum (COSY) for the HMW fraction of the Dammar resin is shown in Figure 6. From the two dimensional NMR spectrum it is possible to determine the association of protons in the one dimensional spectrum.

It is clear from the detailed NMR studies presented here that the HMW polymer isolated from Dammar resin is not purely polycadinene. By examination of the olefinic region, we observe at least four peaks indicating four different environments where only two would be expected in a pure polymer of polycadinene. Integration of these peaks indicates that approximately 1.5 olefins are present per 15-carbon unit, and we would expect 2 such carbons in the pure polymer. The aliphatic region contains many more peaks than would be expected for pure polycadinene. These results suggest that the polymer from Dammar resin is not represented by a pure polycadinene structure. We suggest that the general structural makeup of the polymer is similar to the polycadinene structure but that only two of three units contain olefinic carbons, the other is fully saturated. In addition, on average the olefinic carbons in two units containing such carbons are not at the same site in the structure. This would account for four peaks being present in the NMR spectra. The structure shown in Figure 4 depicts our model for polycadinene structures which comprise sesquiterpenoid resins.

References

1. Dyrkacz, G. R., Horwitz, E. P., *Fuel*, **61**, 3, 1982.
2. Dyrkacz, G. R., Bloomquist, C. A. A., and Ruscio, L., *Fuel*, **63**, 1367, 1984.
3. Greenwood, P. F., Zhang, E., Vastola, F. J. and Hatcher, P. G., *Anal. Chem.*, **65**, 1937, 1993.
4. Stout, S. A. and Hall, K. J., *J. Anal. Appl. Pyrol.*, **21**, 195, 1990

- 5 Stout, S. A., Boon, J. J. and Spackman, W., *Geochim. Cosmochim. Acta*, **52**, 405, 1988.
- 6 Hatcher, P. G., *Organic Geochemistry*, **16**, 959, 1990.
- 7 Faulon, J. L. and Hatcher, P. G., *Energy & Fuels* (in press).
- 8 Hatcher, P. G., Wenzel, K. A. and Faulon, J.-L., Preprints, American Chemical Society Fuel Division, **38**, 1270, 1993.
- 9 Langenheim, J. H. *Science*, **163**, 1157, 1969.
- 10 Brooks, J. D. and Stevens, J. R., *Fuel*, **46**, 13, 1967.
- 11 Cunningham A., Gay, I. D., Oehschlanger, A. C., and Langenheim, J. H., *Phytochem*, **22(4)**, 965, 1983.
- 12 Wilson, M. A., Collin, P. J., Vassallo, A. M., and Russel, N. J., *Org. Geochem.*, **7(2)**, 161, 1984.
- 13 Anderson, K. A., Botto, R. E., Dyrkacz, G. R., Hayatsu R., and Winans, R. E., *Fuel*, **69**, 934, 1990.
- 14 Thomas, B. R., *Organic Geochemistry - Methods and Results*, Springer-Verlag, 599-618, 1969.
- 15 Carman, R. M., Cowley, D. E., and Marty, R. A., *Aust. J. Chem.*, **23**, 1655, 1970.
- 16 Beck, C. W., *Appl. Spec. Rev.*, **22(1)**, 57, 1986.
- 17 Vassallo, A. M., Liu, Y. L., Pang, L. S. K., and Wilson, M. A., *Fuel*, **70**, 635, 1991.
- 18 Wilson, M. A., Hanna J. V., Cole-Clarke, P. A., Greenwood, P. F., and Willett, G. D., *Fuel*, **71**, 1097, 1992.
- 19 Wilson, M. A., Hanna J. V., Cole-Clarke, P. A., Willett G. D., and Greenwood, P. F., *Org. Geochem.*, **18(4)**, 555, 1992.
- 20 Anderson, K. B., Winans R. E., and Botto R. E., *Org. Geochem.*, **18(6)**, 829, 1992.
- 21 Challinor, J. M., *J. Anal. Appl. Pyrol.*, **16**, 323, 1989.
- 22 Nobes, E. D., *Trans. R. Soc. South Aust.*, **46**, 528, 1992.
- 23 Suggate, R. P., *N.Z.J. Sci. Technol.*, **B31(4)**, 1, 1950.
- 24 Grimalt J. O., Simoneit, B. R. T., Hatcher, P. G., and Nissenbaum A., *Org. Geochem.*, **13**, 677, 1988.
- 25 van Aarssen, B. K. G., and Deleeuw, J. W., *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, **36(2)**, 774, 1991.
- 26 van Aarssen, B. K. G., and Deleeuw, J. W., *Geochem. Cosmochim. Acta.*, submitted for publication, 1992.
- 27 Clifford, D. J., and Hatcher, P. G., *Org. Geochem.*, submitted for publication, 1993.
- 28 Wenkert, E., and Buckwalter, B. L., *J. Am. Chem. Soc.*, **94(12)**, 4367, 1972.
- 29 Lambert, J. B., and Frye, J. S., *Science*, **217**, 55, 1982.
- 30 van Aarssen, B. G. K., Cox, H. C., Hoogendoorn, P., and de Leeuw, J. W., *Geochem. Cosmochim. Acta.*, **54**, 3021, 1991.
- 31 Crelling, J. C., Pugmire, R. J., Meuzelaar, H. L. C., McClennen, W. H., Huai, H. and Daras, J., *Energy & Fuels*, **5**, 688, 1991.
- 32 Meuzelaar, H. L. C., Huai, H., Lo, R. and Dworzanski, J. P., *Fuel Proc. Technol.*, **28**, 119, 1991.
- 33 Clifford, D. J., Hou, L., Bortiatynski, J. M. and Hatcher, P. G., Technical Progress Report February - 1993, Prepared for the U.S. DOE under Contract No. DE-FG22-92PC92104.
- 34 Hou L., Clifford, D. J., Bortiatynski, J. M., and Hatcher, P. G., Technical Progress Report October - 1993, Prepared for the U.S. DOE under Contract No. DE-FG22-92PC92104.

Table 1. Ultimate analysis (DMMF) of the HMW fraction from a Dammar resin, the resinite from a Blind Canyon coal sample, and pure polycadinene.

Sample	% C	% H	% O	Monomeric Formula
HMW polymer (Dammar)	84.2	11	4.8	C ₁₅ H ₂₄ O _{0.65}
Whole resinite (DECS16)	86.2	10.4	3.4	
Polycadinene (pure polymer)	87.3	12.7	0	C ₁₅ H ₂₆

*Obtained by difference.

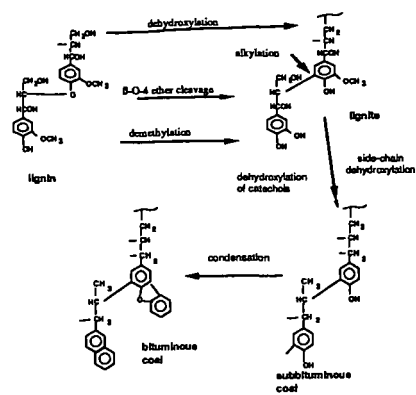


Figure 1. Sequence of reactions proposed for the coalification of lignin in wood to coalified wood of the rank of bituminous coal.

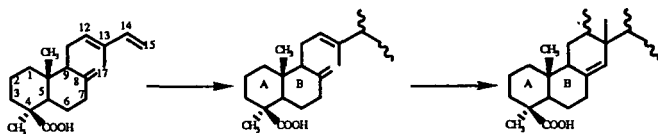


Figure 2: Polymerization of communic acid to *trans*-14,15-polycommunic acid followed by the intramolecular cyclization of carbons 17 and 13.

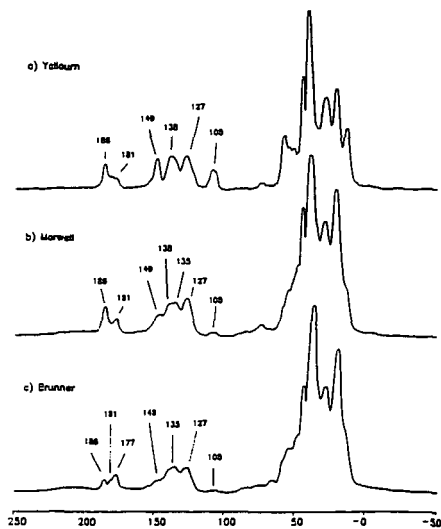


Figure 3: ^{13}C CPMAS NMR of diterpenoid resinites.

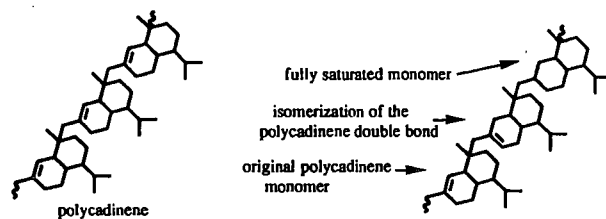


Figure 4: Polycadinene polymer and polymer containing possible transformations of the cadinene monomers.

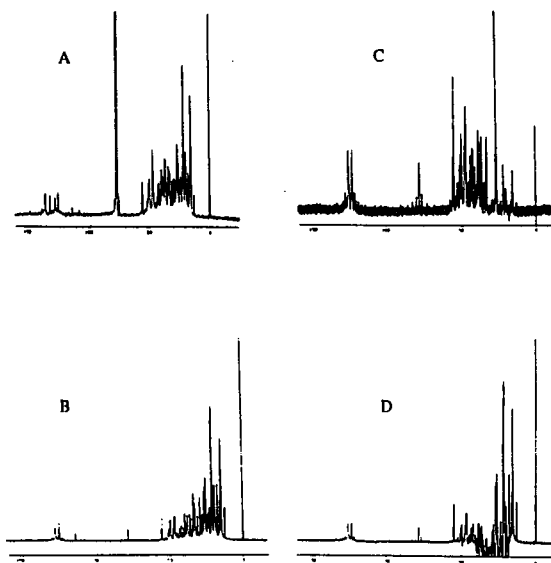


Figure 5: ^{13}C broadband decoupled (A), 45° DEPT (B), 90° DEPT (C), and 135° DEPT (D) NMR spectra of HMW fraction of Dammar resin in CDCl_3 .

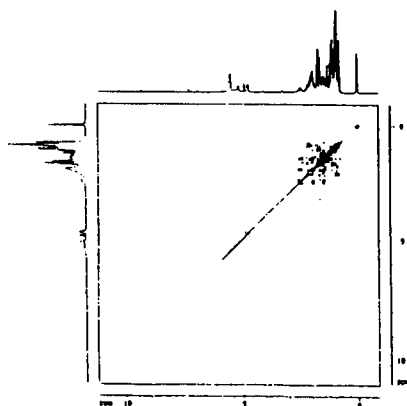


Figure 6: ^1H - ^1H correlation spectrum (COSY 45°) of the high molecular weight fraction of the Dammar resin in CDCl_3 .